# POSTER

## STUDY OF THE BEHAVIOUR OF PETROLEUM COKE AS AN ADDITIVE IN COKEMAKING

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### INTRODUCTION

The use of green petroleum coke as an additive in industrial coal blends is a practice often used by steel companies, depending on its availability in the market at lower prices than coking coals. Improvements in metallurgical coke quality when petroleum coke is used as additive can be achieved by selecting the type and characteristics of the petroleum coke (1-3).

The objectives of this work were to get knowledge about the role of petroleum coke added to the coal/coal blend by means of characterization using non-conventional techniques and to study variations in metallurgical coke quality in relation to the properties of petroleum coke added. Some of the analytical methods/techniques used for characterization and chemistry of carbon materials, such as FTIR, hydrogen donor ability, free swelling index and thermogravimetric analysis, have been successfully adapted in the characterization of petroleum coke.

### EXPERIMENTAL

Table 1 shows the typical properties of a set of five green petroleum cokes and one calcined petroleum coke (R4).
*Optical microscopy.* Quantitative assessments of optical texture composition were made by means of a point counting technique, using a polarized light microscope. The nomenclature used has been described previously (2) and a category including mesophase spheres within an isotropic matrix (MI) was also quantified.
*FTIR spectroscopy.* FTIR spectra were recorded by using standard petroleum coke:KBr pellets at 1:100 ratio.
*Hydrogen donor ability (Da).* Mixtures of petroleum coke and anthracene (1:1 w/w) were heated in sealed glass tubes under argon atmosphere to 450 °C at a rate of 5 °C/min (4,5). After heating, the $CS_2$ extracts were analyzed by capillary gas chromatography (5).
*Thermogravimetric analysis.* TGA measurements were performed on samples ($<125$ $\mu$m) heated to 1000 °C at a rate of 30 °C/min flowing nitrogen at 50 ml/min.
*Free swelling index (FSI).* A sample ($<212$ $\mu$m) was heated in a crucible to 820 °C for 2.5 min. The profile of the coke residue was compared to standard profiles (ISO 501-1980).
*Testing the effect of adding petroleum coke.* Blends of a low-volatile bituminous coal *(VM: 18.5 wt% db; ash: 8.0 wt% db; Gieseler maximum fluidity (MF): 21 ddpm; $R_o$: 1.37 %)* and petroleum coke were prepared and then subjected to the Gieseler plasticity test (ASTM D2639-74). The blends (400 g) were carbonized in a laboratory-scale oven (6) under $N_2$ atmosphere at a heated rate of 5 °C/min until the top of the charge was 1000 °C. Resultant cokes were subjected to an abrasion test and reactivity to $CO_2$ -ECE method- (6).

### RESULTS AND DISCUSSION

The green petroleum cokes selected cover a narrow range in volatile matter content (10-14 wt% db) and a wide range in sulphur content (0.82 and 4.57 wt% db).

**Table 1.** Main characteristics of petroleum cokes.

| Petroleum coke | R2 | RD | R1 | EH | R3 | R4 |
|---|---|---|---|---|---|---|
| Ash (wt% db) | 0.9 | 0.3 | 0.4 | 0.6 | 0.4 | 0.0 |
| VM (wt% db) | 14.4 | 10.3 | 12.7 | 12.5 | 11.9 | 0.4 |
| S (wt% db) | 2.69 | 0.82 | 4.57 | 1.33 | 4.08 | 0.00 |
| C (wt% db) | 90.3 | 93.6 | 88.2 | 90.1 | 90.1 | 99.8 |
| H (wt% db) | 4.2 | 3.0 | 3.9 | 4.3 | 4.3 | 0.1 |
| N (wt% db) | 1.3 | 1.1 | 1.6 | 2.2 | 0.6 | 0.0 |

Optical texture composition is given in Table 2. With the exception of R3 and R4, the presence of unreacted isotropic and mesophase spheres within an isotropic matrix (MI) can be observed. This suggests that green petroleum coke has not been completely carbonized in the coker. These components offer a potential source of volatile matter release in the transition to anisotropic features when these types of petroleum cokes are used as an additive in cokemaking. If so, petroleum coke could modify physical and chemical mechanisms during carbonization. In an attempt to demonstrate the "activity" of the above components a characterization using FTIR, $D_a$, TG and FSI tests was carried out (Table 3).

The aliphatic hydrogen content (Hal) decreases with a decrease in the methylene groups evaluated by the H1375/H1440 ratio ($CH_3:CH_2$ groups ratio). A good correlation between Hal and H1375/H1440 ratio was found (r=0.984). From FTIR data an increasing order of carbonization degree can be established:

$$R2 < RD < R1 < EH < R3 < (R4)$$
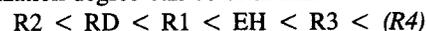
It is obvious that R4 has the highest carbonization degree. The $CH_2$ groups detected must exist in the form of $CH_2$ bridges and in hydroaromatic systems. From the data of the H1375/H1440 ratio it can be deduced that the most abundant aliphatic groups in petroleum cokes with lower Hal are $\alpha$-$CH_3$ groups. The presence of hydroaromatic systems in petroleum cokes can explain the activity found in hydrogen transfer reactions with anthracene as an acceptor ($D_a$) at 450 °C (Table 3). The lower the H1375/H1440 ratio the lower the $D_a$ ($r = -0.921$).

**Table 2.** Optical texture composition of petroleum cokes.

| Petroleum coke | R2 | RD | R1 | EH | R3 | R4 |
|---|---|---|---|---|---|---|
| Mosaic | 15.2 | 11.6 | 26.8 | 59.1 | 8.6 | 7.6 |
| Small domain | 25.5 | 26.3 | 32.6 | 27.7 | 43.4 | 0.0 |
| Domain | 21.2 | 38.4 | 28.0 | 4.8 | 45.5 | 41.3 |
| Flow domain | 12.5 | 21.0 | 8.9 | 1.0 | 2.6 | 51.5 |
| Isotropic | 12.8 | 0.4 | 0.6 | 3.8 | 0.0 | 0.0 |
| MI | 12.8 | 2.3 | 3.1 | 3.6 | 0.0 | 0.0 |

**Table 3.** Non-conventional data of petroleum cokes.

| Petroleum coke | R2 | RD | R1 | EH | R3 | R4 |
|---|---|---|---|---|---|---|
| Har | 0.22 | 0.26 | 0.26 | 0.32 | 0.40 | - |
| Hal | 0.78 | 0.74 | 0.74 | 0.68 | 0.60 | - |
| H1375/H1440 ratio | 0.86 | 0.90 | 0.90 | 0.97 | 1.00 | - |
| $D_a$ (mg H/g coke) | 0.56 | 0.44 | 0.25 | 0.19 | 0.10 | 0.00 |
| VM400-500 (wt%) | 4.12 | 3.49 | 2.98 | 1.75 | 1.45 | 0.02 |
| Tmax | 503 | 525 | 548 | 621 | 644 | - |
| FSI | 1 | ½ | ½ | 0 | 0 | 0 |

The amount of volatile matter released between 400 and 500 °C ($VM_{400-500}$) is also consistent with the above order of carbonization degree established from FTIR and $D_a$ data. A linear relationship ($r = -0.994$) exists between the amount of $VM_{400-500}$ and the temperature of maximum evolution of volatiles (Tmax). For higher $VM_{400-500}$ the maximum evolution of volatile species occurs at a lower temperature during pyrolysis.

FSI data are also consistent with the order of the carbonization degree proposed. R2, with a lower carbonation degree, gives a residue with a certain degree of agglomeration (FSI = 1). RD and R1 have a lower ability to agglomerate. Finally, EH, R3 and R4 with a higher carbonization degree give a pulverulent residue.

*Testing the effect of adding petroleum coke*
The addition of petroleum coke to a low-volatile bituminous coal leads to a lower maximum fluidity, MF, (Figure 1) accompanied by a decrease in the fluid range. In addition, a good relation between the order in decreasing MF and the carbonization degree of the petroleum coke added can be observed.

Coke quality parameters such as abrasion index and reactivity to $CO_2$ improve with petroleum coke addition, also following the order established for the carbonization degree of the petroleum coke added (Figure 2).

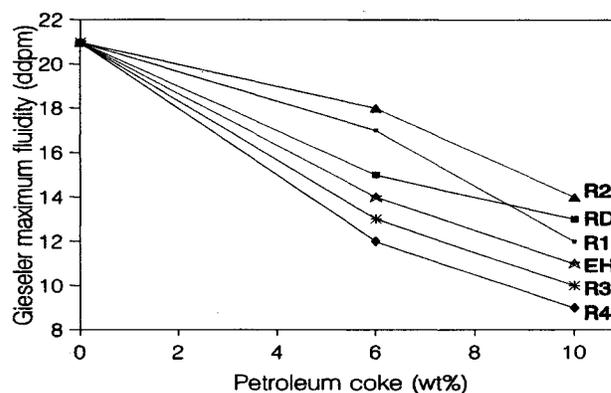
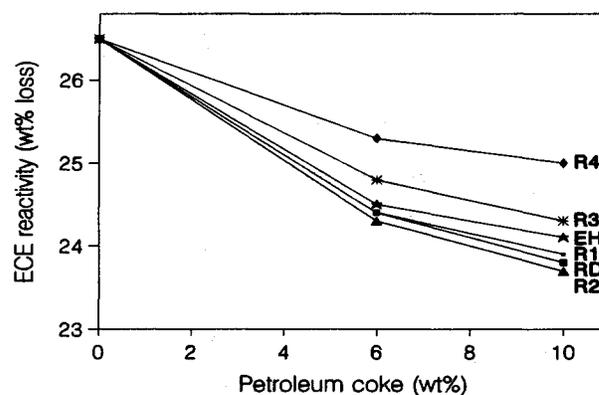**Figure 1.** Variation of Gieseler maximum fluidity with the type of petroleum coke.


**Figure 2.** Variation in ECE reactivity of metallurgical cokes.

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